

DIRECT SYNTHESIS OF ALCOHOL FUELS OVER MOLYBDENUM-BASED CATALYSTS

Kamil Klier, Richard G. Herman, Gary W. Simmons, and Charles E. Lyman
with
Mieczyslawa Najbar, Roy Bastian, and José G. Santiesteban

Zettlemoyer Center for Surface Studies
and
Department of Chemistry
Lehigh University
Bethlehem, PA 18015

For presentation at the
Eighth Indirect Liquefaction Contractors' Review Meeting
Pittsburgh Energy Technology Center
Pittsburgh, PA

November 15-17, 1988

PREPARED FOR THE UNITED STATES
DEPARTMENT OF ENERGY

Under Contract No. DE-AC22-85PC80014
September 25, 1985-December 24, 1988

ABSTRACT

The first part of this research project involved the study of alkali/MoS₂ and alkali/Co/MoS₂ catalysts so that the scientific understanding of the functioning of these catalysts could be used to optimize the production of linear alcohols from low H₂/CO ratio synthesis gas. Most of the results of this research were summarized in the 1988 release of the "Proceedings of the 7th Indirect Liquefaction Contractors' Review Meeting-Volume II." More recent conclusions concerning the surface state of these catalysts and the surface chemistry involved in the synthesis of C₁-C₄ alcohols over these catalysts will be presented in the final report for this research project, which will be submitted in December 1988. Of special interest note is the mechanistic information obtained by ¹³C NMR analysis of the products formed upon passing a ¹³CH₃OH/H₂/CO reactant mixture over the catalyst under normal alcohol synthesis conditions, which showed that ethanol was formed via classical CO insertion into a methyl intermediate derived from methanol that was bound to the catalyst surface.

In studying the selective oxidation of methane to oxygenates, it was observed that the presence of chlorine tended to enhance the yield of partial oxidation products. To probe the effect of chlorine on the activity and selectivity observed with a 4.8 wt% Pd/SiO₂ catalyst, dichloromethane was added to a methane/oxygen reactant mixture. The composition of the gas mixtures used were CH₄/O₂/CH₂Cl₂ = 1/2/0.2 and 1/2/0.015, and the volume of the gas mixture injected into a helium carrier gas as a pulse was 0.975 cm³. It was observed that the presence of dichloromethane caused a decrease in the amount of methane converted to products and an enhancement in the partial oxidation products formed. The products formed in the presence of dichloromethane were formaldehyde and chloromethane, in addition to the

carbon dioxide that was formed in high yields in the absence of the dichloromethane. Even after the addition of dichloromethane was terminated, chloromethane was formed during pulsing of the methane/oxygen mixture, showing that there was still chlorine on the surface of the catalyst. The presence of water in the reactant mixture inhibited the conversion of methane to products. Sequential pulsing experiments demonstrated that optimum surface concentrations of chlorine and oxygen exist for the partial oxidation of methane over this palladium catalyst. This conclusion for the oxygen surface coverage was reinforced by an experiment in which methane was pulsed over an oxygen-saturated surface, where the conversion of methane to carbon dioxide passed through a maximum that indicated a direct dependence on the oxygen coverage of the surface.

A newly prepared 1.0 wt% Pd/SiO₂ catalyst was tested under *continuous flow* steady-state conditions for methane conversion to oxygenates from a CH₄/air ≈ 1.0/1.1 reactant feed at ambient pressure in a microreactor. Methane activation was observed to occur at temperatures as low as 548K. Although carbon monoxide and hydrogen were among the products formed, the major oxidation product was carbon dioxide. Addition of a rather large amount of water to the reactants (O₂/H₂O ≈ 3/1) resulted in enhanced yields of CO, although appreciably higher temperatures were required to activate the methane under these conditions. Addition of dichloromethane, instead of water, to the CH₄/O₂ reactants (O₂/CH₂Cl₂ ≈ 6/1) greatly suppressed the oxidation of methane, and a temperature of about 773K was required to observe the initiation of methane oxidation. Under these latter conditions, the predominant reactions were conversions of the injected dichloromethane to CH₃Cl at low temperatures and to CO₂ and HCl at high temperatures.

Dichloromethane behaved as a retardant when added in such large amounts to the CH_4/O_2 reactant mixture.

The 1.0 wt% Pd/SiO₂ catalyst (1 g diluted with Pyrex beads) was also tested in the *high pressure continuous flow* reactor for methane conversion to oxygenates from a $\text{CH}_4/\text{air} = 50/50$ reactant mixture at ambient pressure (0.1 MPa) and at 5.0 MPa (50 atm). At 623K, 100% of the O_2 was converted to CO_2 and H_2O at both pressures, and selective oxidation products were not detected. The same behavior was observed at higher temperatures up to 723K.

The decomposition of methanol, a possible transient product of the methane oxidation reaction under these conditions, was studied over a fresh portion of the Pd/SiO₂ catalyst in the temperature range of 423-648K at 0.1 MPa and at 5.0 MPa. In these experiments, 0.035 to 0.140 mol methanol/hr was injected into a stream of nitrogen with GHSV = 3,000-12,000 l(STP)/kg cat/hr (0.123-0.492 mol nitrogen/hr). At 0.1 MPa, the decomposition of methanol approached 100% at temperatures >573K. At the higher pressure of 5.0 MPa, the decomposition of methanol was suppressed so that only about 50% of the methanol was decomposed into synthesis gas at 573K. The influence of flow rate on the decomposition of methanol was also studied, and it was observed that as the flow rate of both the methanol and the nitrogen carrier gas were increased at 598K and 5.0 MPa, the % conversion decreased but the yield of CO increased slightly.

In summary, it has been shown that the Pd/SiO₂ catalyst is an active catalyst for the oxidation of methane under mild reaction conditions, e.g. ambient pressure and <773K. It appears that the active catalyst surface exists in an intermediate oxidation state, e.g. not as exposed Pd(O) surface nor as uniform PdO. Addition of small amounts of dichloromethane to the reactant mixture increased the selectivity to partial oxidation products,

i.e. oxygenates other than CO_2 such as HCHO and CO, while decreasing the methane conversion. The presence of water in the reactant mixture induces a similar behavior. The presence of too much H_2O or CH_2Cl_2 in the reactants greatly suppressed the overall catalytic activity, and higher reaction temperatures were needed to observe appreciable degrees of conversion of methane. At the same time, however, at the higher temperatures the selectivity toward partial oxidation products decreased. These studies indicate that for the selective formation of partial oxidation products from methane over palladium catalysts, there are optimum surface concentrations of chlorine and oxygen. In examining the decomposition of methanol, one of the desirable partial oxidation products, over Pd/SiO_2 catalysts in a large volume reactor, it was shown that elevated pressure and gas flows decreased the rate of decomposition of methanol. Therefore, reaction engineering of the oxidation of methane over palladium-based catalysts should be carried out such that the yields of selective oxidation products can be enhanced by balancing the reaction temperature with surface reactant and promoter concentrations, pressure, and reactant gas flow.

INTRODUCTION

The objective of this research project is to develop the scientific data for a catalytic process for the direct selective conversion of hydrocarbon fuel. The desired process will convert light hydrocarbons (C_1 - C_4), in the presence of or absence of carbon-rich synthesis gas, to liquid alcohol fuels that would be utilized as neat fuels and as high octane blending agents with hydrocarbon fuels. To establish the foundation for such a process, this research involves the preparation, catalytic testing,

and characterization of alkali/MoS₂ catalysts that sometimes contain additional promoting or stabilizing components.

The two principal goals initially addressed are:

- (i) to understand the functioning of alkali/MoS₂ catalysts in alcohol synthesis (known as the Dow Technology, but patents have also been filed by Union Carbide) and to optimize the activity of these catalysts for high yields of fuel alcohols from low H₂/CO ratio synthesis gas, and
- (ii) to develop a molybdenum oxide-based catalyst or a silica-based catalyst containing Pd, Rh, or Pt for the selective oxidation of methane to methanol or formaldehyde at elevated pressures. Upon evaluation of the molybdenum oxide catalysts, however, it was determined that these were not prospective for selective methane oxidation at temperatures below 773K and further investigations centered on supported palladium catalysts.

A task to be accomplished at a later stage in this research will utilize and build upon the data and principles derived from the two initial tasks and will be directed

- (iii) to explore and develop novel multi-component molybdenum-based catalysts for the conversion of light hydrocarbons and synthesis gas to liquid alcohol fuels.

An auxiliary task of this research project that will provide detailed scientific information concerning the structure and function of the heterogeneous catalyst, as well as the crystal and defect structures that maintain the active catalyst and make it selective and durable under synthesis conditions, will be achieved by

- (iv) fully characterizing the viable catalysts by modern methods of electron microscopy and optical and electron spectroscopy.

TECHNICAL PROGRESS

Synthesis of Alcohols from Synthesis Gas over MoS₂-based Catalysts

During this research project, the two classes of MoS₂-based catalysts that were investigated for alcohol synthesis were (i) the binary alkali/MoS₂ catalysts and (ii) the ternary alkali/Co/MoS₂ catalysts, where the alkali = K or Cs. The preparation and catalytic testing (using H₂/CO = 1 synthesis gas) of these catalysts has been described in detail in the proceedings of the previous DOE/PETC contractors' meeting (1) and will not be repeated here. A brief consideration of the surface state of the catalyst was also given, and the results obtained by injecting methanol and ¹³C-enriched methanol into the synthesis gas over the 20 wt% CsOOCH/MoS₂ catalyst and the K₂CO₃/(Co/MoS₂) = 10/90 wt% catalyst were presented. It was observed that the terminal carbon of ethanol was exclusively enriched and that the methyl group of methyl acetate was preferentially enriched, where the product analyses were carried out by ¹³C nuclear magnetic resonance (NMR). These isotopic studies showed that the formation of ethanol occurred through CO insertion into a methyl intermediate bound to the surface to form an acyl precursor that was hydrogenated to produce ethanol. The methyl intermediate clearly was derived from an oxygenated species since only the terminal carbon of ethanol was enriched. These studies also indicate that the methyl ester was formed by CO insertion into an intermediate, such as a methoxy anion, derived from the injected labeled methanol. The results of the isotopic study have been presented and discussed elsewhere (2-3). Of special note is the stability of these catalysts and the lack of deactivation induced by the presence of iron carbonyl in the reactants (4).

The studies of these catalysts that were carried out during this project has confirmed that rather large quantities of alkali must be added to MoS₂ catalysts in order to shift the selectivity from hydrocarbons to alcohols. It has also demonstrated that

- (i) the alkali/MoS₂ catalysts are bifunctional in nature,
- (ii) linear alcohols are produced by a 'classical' mechanism that proceeds via stepwise insertion of CO into alkyl-metal center bonds,
- (iii) the presence of cobalt greatly enhances the C₁ → C₂ homologation step that leads to ethanol as a dominant product,
- (iv) methane is formed predominantly as a secondary product over these promoted catalysts, and
- (v) the synthesis patterns over the alkali/(Co)MoS₂ catalysts that maximize ethanol are opposite to those observed with the Cs/Cu/ZnO catalyst, which minimizes the formation of ethanol due to chain growth by rapid beta addition (to the β-carbon) rather than CO addition.

Selective Oxidation of Methane to Oxygenates over Pd/SiO₂ Catalysts

In the present work, Pd/SiO₂ catalysts were investigated for the partial oxidation of methane. Reactions that were observed included the oxidation of methane to formaldehyde [1] and the oxidation to synthesis gas [2].



Among the undesirable side reactions is the full oxidation of the methane [3], and the selectivity is usually measured in terms of the yields produced



by reaction [1] or reaction [2] relative to [1] + [2] + [3]. No methanol formation was observed over the present catalysts under the reaction conditions that were employed.

In studying the reactivity and selectivity of various metal oxide catalysts for the oxidative coupling of methane to C₂ hydrocarbons, it was observed by others (5) that addition of chlorides to the catalysts or addition of small amounts of HCl to the methane reactant mixture made the catalysts more selective. In very early studies of methane oxidation, it was noticed that the addition of HCl to the reactant gas mixture increased the selectivity toward formaldehyde over iron, tin, and aluminum phosphate catalysts (6) and over lead oxide catalysts (7). Later, Cullis et al. (8) and Mann and Dosi (9) found that the presence of halogenides of methane in CH₄/O₂ mixtures enhanced the selectivity of Pd catalysts to formaldehyde. It had been postulated earlier that dichloromethane dissociated on the surface of palladium catalysts (10), and it has now been clearly shown that dichloromethane dissociates on the Pd(100) surface (11-13).

Pulsed Reactor Studies with a 4.8 wt% Pd/SiO₂ Catalyst. To explore the role of chlorine and chlorine-containing compounds on the activity and selectivity of converting methane to formaldehyde over the 4.8 wt% Pd/SiO₂ catalyst that was used during the previous year of research (1,14,15), a number of runs were carried out in which dichloromethane was added to a CH₄/O₂ = 1/2 reactant feed carried in a helium carrier gas. The stainless steel 0.64 cm o.d. reactor employed was 23 cm in length and was encased in a bronze block that provided for isothermal operation of the reactor. The catalyst was placed approximately 3 cm above the reactor outlet, and an

axially positioned thermocouple was centered in the bed.

For these studies, the gas handling system was modified so that a $\text{CH}_4/\text{O}_2/\text{N}_2$ mixture could be fed into the reactor in 0.975 cm^3 pulses rather than in sequential neat 0.1 cm^3 pulses of CH_4 and O_2 , as used previously (1,14,15). A schematic of the reactor/chromatographic system is shown in Figure 1. Valve I was controlled by a Valco Instruments Co. digital valve sequence programmer that provided for injection of a reactant pulse into the He carrier gas every 20 min. In addition, Valve A and a liquid bubbler were placed in the methane gas line so that CH_2Cl_2 could be added in measureable quantities. The quantity of dichloromethane added to the methane stream was controlled by the temperature of the bubbler and the methane gas passing through it. The temperatures used in this studies were 273K and 233K (-40°C). The flow rate of the N_2 component was adjusted to match that of the CH_2Cl_2 additive that was added when the methane conversion was at steady state. Upon addition of the CH_2Cl_2 , the N_2 flow was terminated so that the overall flow rate of the reactant gas stream entering the reactor was not altered.

After loading the catalyst into the reactor, a flow of N_2 was established ($52 \text{ cm}^3/\text{min}$) at a pressure of 545 kPa. The catalyst was then pretreated at 813K with 150 consecutive pulses of methane. The X-ray diffraction powder pattern, shown in Figure 2, of a catalyst treated in the same way demonstrated that Pd(0) was the crystalline phase present. After cooling the catalyst to 648K in a flow of He and reducing the pressure to 250 kPa, pulses of $\text{CH}_4 + \text{O}_2 + \text{N}_2$ (1/2/0.2) were passed over the catalyst until a constant level of methane conversion was obtained.

Six consecutive pulses of $\text{CH}_4 + \text{O}_2 + \text{CH}_2\text{Cl}_2$ (1/2/0.2) were then introduced over the catalyst. A large drop in methane conversion occurred,

and, as indicated in Figure 3, a decrease in selectivity to CO_2 also was observed. With the addition of dichloromethane to the reactant pulses, formaldehyde and chloromethane were formed over the catalyst. When the dichloromethane was replaced by nitrogen, the formation of formaldehyde ceased.

After this experiment, the catalyst was cleaned at 813K via extensive pulsing of $\text{CH}_4 + \text{O}_2$ (1/2) and then cooled to 761K for additional pulsing experiments. This "cleaned" catalyst was still releasing a small quantity of chloromethane and the CH_4 conversion was appreciably less than that observed with the freshly treated catalyst. The following pulsing sequence was carried out over the "cleaned" catalyst:

<u>Pulses</u>	<u>Reactant</u>
Four	$\text{CH}_4 + \text{O}_2 + \text{CH}_2\text{Cl}_2$ (1/2/0.015)
One	$\text{CH}_4 + \text{O}_2$ (1/2)
Two	CH_4
Five	$\text{CH}_4 + \text{O}_2$ (1/2)
Two	$\text{CH}_4 + \text{N}_2$ (1/2).

The results are shown in Figure 4, where it is seen that the initial trends for chloromethane and formaldehyde follow those observed in Figure 3. However, the response to the dichloromethane pulses is much more rapid (sharper maxima in the yield curves) in this case even though the amount of dichloromethane to which the catalyst was exposed in each pulse was much less. It is clear that the two pulses of methane resulted in enhanced removal of chlorine and oxygen from the catalyst surface, while subsequent pulsing of methane and oxygen tended toward a steady state reactivity. However, subjecting the catalyst to pulses of methane and nitrogen suppressed the formation of chloromethane while increasing the production of CO_2 . These results indicate that oxygen in the $\text{CH}_4 + \text{O}_2$ pulses was steadily replacing chlorine in or on the catalyst, while this could not occur with

the $\text{CH}_4 + \text{N}_2$ pulses. During the latter pulses, however, reactive surface oxygen was reacting with the methane to form carbon dioxide.

The experiment was continued by lowering the reaction temperature to 648K and pulsing $\text{CH}_4 + \text{O}_2$ (1/2) over the catalyst until a constant conversion of methane was achieved. The methane reactant was then passed through a water-filled bubbler so that a $\text{CH}_4 + \text{O}_2 + \text{H}_2\text{O}$ (1/2/0.024) gas mixture was produced. Four pulses of this reactant mixture were passed over the catalyst, and Figure 5 shows that the presence of water inhibited the formation of both carbon dioxide and chloromethane. Presumably, water was competitively adsorbing on the catalyst and was blocking the adsorption and activation of methane since both products were inhibited.

These experiments show that there are optimum surface concentrations of chlorine and of oxygen, as well as methane, for the oxidation of methane at temperatures less than 773K. For the selective oxidation of methane to formaldehyde, Figures 3 and 4 show that once an optimum Cl surface coverage is established, only a small amount of chlorine in the gas phase would be sufficient to maintain the desirable surface coverage. In the current experiments, excess chlorine via dichloromethane was present so that the oxidation activity of the catalyst was suppressed, but both carbon dioxide and formaldehyde were present in the exit gas. However, when the dichloromethane injection was terminated but the $\text{CH}_4 + \text{O}_2$ flow was maintained, only carbon dioxide (no formaldehyde) was detected as an oxidation product. In the experiment described by Figure 4, the surface of the catalyst during pulses 8-12 must have had a high coverage of chlorine and oxygen, and the gas phase oxygen in the methane/oxygen pulses must have adsorbed competitively with the methane since the reactivity of the methane was much higher when gas phase oxygen was not present (pulses 13 and 14).

An additional experiment demonstrated this more clearly. Another portion of the Pd/SiO₂ catalyst was loaded into the reactor and, after reduction by many pulses of methane, was treated with pulses of oxygen introduced into the N₂ carrier gas (flow rate = 52 cm³/min) at 544K. Nine pulses of methane were then passed over the catalyst, and the observed methane conversion to carbon dioxide is shown in Figure 6. It is evident that little of the methane was oxidized over the oxygen-covered Pd catalyst, but as the oxygen was gradually depleted from the surface the amount of methane that was activated and oxidized increased, passed through a maximum, and then decreased. This result supports the hypothesis that there is an optimum surface coverage of oxygen that provides for the adsorption, activation, and subsequent reaction of methane with the surface oxygen.

Continuous Flow Reactor Studies with a 1.0 wt% Pd/SiO₂ Catalyst. The catalyst that was tested during this phase of the research was a 1.0 wt% Pd/SiO₂ catalyst that was prepared by impregnation of Davisil silica (Grade 636, reported to have a surface area of 480 m²/g) with palladium acetate. The palladium acetate (0.1055 g) was dissolved in 0.4 l of acetone, which was then mixed with 5.0 g of the silica. The resultant slurry was allowed to equilibrate for 16 hr in a fume hood, and it was then heated quickly under flowing nitrogen to boiling and quickly removed from the heat source. Complete drying occurred in 2.5-3.0 min, and the resultant yellow-orange powder had a 6.0 nm SiO₂ crystallite size as determined by X-ray powder diffraction analysis.

The prepared catalyst, consisting of Pd(OAc)₂/SiO₂ (0.12 g), was loaded into the stainless steel microreactor and was initially decomposed in a flow of helium (3 cm³/min) at 363K (90°C) for 15 hr, and then the temperature was

increased to 423K (150°C) for 2 hr. The decomposition of the acetate was monitored by on-line gas chromatographic analyses. After the decomposition, oxygen (75 cm³/min) was passed over the catalyst at 423K for 1 hr to remove any residual carbon, and then the catalyst was reduced with hydrogen (3 cm³/min) at 423K until no further generation of water was noted by GC analysis of the exit gas.

The methane that was utilized for these experiments was obtained from MG Industries and was of ultra high purity (99.97%). The zero-grade air was a synthetic O₂/N₂ mixture obtained from Air Products and Chemical, Inc. (total hydrocarbons < 0.5 molar ppm). Product analyses were achieved by simultaneous on-line injection into parallel columns consisting of a 10 m x 0.32 mm Poraplot Q coated fused silica capillary GC column and a 1 m x 3.2 mm packed 13X zeolite column in a Hewlett-Packard Model 5890 gas chromatograph interfaced with a 3393A integrator.

The testing program consisted of the following five steady state runs where the temperature was varied in the range of 473 to 773K:

- 1) CH₄/Air = 1.0/1.1 with a total flow of 170 cm³/min,
- 2) CH₄/Air = 1.0/1.1 plus water addition corresponding to 6.8 cm³/min of gaseous water,
- 3) CH₄/Air = 1.0/1.1 plus CH₂Cl₂ addition corresponding to 3.4 cm³/min of gaseous dichloromethane,
- 4) CH₄/Air = 1.0/1.1 plus the simultaneous addition of H₂O and CH₂Cl₂, and
- 5) CH₄/Air = 1.0/1.1 plus CH₂Cl₂ addition corresponding to 3.4 cm³/min of gaseous dichloromethane.

In each experiment, the flow of the CH₄/air reactant mixture was maintained at 170 cm³/min, which produced a GHSV = 85,000 l/kg initial untreated

catal/hr. The "air" composition was that of the synthetic "zero air", 24% O₂ and 76% N₂.

The first test involved sequentially heating the Pd/SiO₂ catalyst from ambient temperature to 673K under a flow of the CH₄/Air = 1.0/1.1 reactant (typically 48% CH₄/12.5% O₂/39.5% N₂). As shown in Figure 7, appreciable oxidation was noted at 548K (275°C) and all of the oxygen was consumed as the reaction temperature approached 623K (350°C). At the higher temperatures, the following reactions can be considered as occurring simultaneously over this active catalyst:



The formation of hydrogen was noted in the product stream at the higher temperatures, but it was not quantified. In addition, Reactions 6 and 7 could also occur over this catalyst.



The CO₂, CO, and H₂O contents in the exit gas are shown in Figure 8. It is evident that Reaction 3 was the predominant reaction occurring under these reaction conditions. However, Reactions 4 and 5 were also occurring. The conversions at each temperature were obtained during steady-state testing of 2-15 hr.

Addition of water (=4 mol%) by means of a Gilson injection pump into the reactant gas mixture (CH₄/O₂/N₂/H₂O = 1.00/0.26/0.84/0.085) resulted in the inhibition of the methane oxidation reaction at the lower temperatures. Figure 9 shows that the methane activation temperature was increased by ≈100K by the water addition. The 773K (500°C) test also demonstrates that

the water addition tended to promote the partial oxidation of methane to CO, as represented by Reaction 4 (again H₂ was observed but not quantified).

Replacing the water injection by addition of dichloromethane to the extent of 2 mole of the total reactant stream (CH₄/O₂/N₂/CH₂Cl₂ = 1.00/0.26/0.84/0.04) demonstrated that dichloromethane was a strong inhibitor of methane oxidation. Figure 10 shows that no appreciable oxidation of methane was observed until the reaction temperature reached 773K (500°C). At this temperature, the dichloromethane was oxidized predominately to HCl and CO₂. The influence of the generated HCl on the GC analysis of the water (and other products) is not known at this time, and therefore the data for this reaction temperature are only approximate.

Addition of both water and dichloromethane to the inlet stream at 773K exhibited an even greater suppression of the conversion of methane. GC/MS analyses of the products collected from the exit stream showed that CO₂, HCl, H₂CO, and CH₃Cl were formed from the reactants in low yields. A subsequent test at 773K was carried out with only 2 mole dichloromethane being added to the CH₄/Air = 1.0/1.1 reactant stream, and the products were collected for GC/MS analysis. Again, CO₂, HCl, H₂CO, and CH₃Cl were observed in small quantities.

Treatment of the tested catalyst with O₂ resulted in a brief generation of a small amount of CO₂ + CO. This indicates that a small amount of carbon was deposited on the catalyst, probably via Reaction 7. Characterization of the Pd/SiO₂ catalyst by X-ray powder diffraction after its testing at 773K for 4 days demonstrated that the palladium crystallite size had increased to a diameter of ≈20 nm.

Using a fresh portion of catalyst, tests designated above as 1), 2), and 3) were repeated using a CH₄/O₂ flow rate of 100 cm³/min rather than 170

cm³/min. All of the results reported above were qualitatively reproduced at this lower gas flow.

Testing a 1.0 wt% Pd/SiO₂ Catalyst in a High Pressure Reaction System.

A new reactor and associated expansion chamber, with a safety rupture disc (rated at ≈12.4 MPa) between the two tubular vessels, has been constructed and tested at elevated pressure for possible gas leaks. A schematic of the reaction system that can be used for testing of methane oxidation catalysts at pressures up to 10 MPa (100 atm) is shown in Figure 11. The cylindrical heater consists of three heating sections so that very good temperature control can be maintained. In the reactor configuration being used, the internal thermocouple is axially centered in the reactor so that the end of the thermocouple is located in the catalyst bed. As with the ambient pressure system, the exit stream is continually analyzed by an on-line Hewlett-Packard GC having an in-line sampling valve. Methanol, carbon monoxide, and nitrogen were quantitatively determined, but the analysis of hydrogen was not carried out.

A 1.0 g portion of the 1.0 wt% Pd/SiO₂ catalyst was diluted with Pyrex beads and loaded into the continuous flow stainless steel reactor. The reactor was purged with flowing methane at ambient temperature and pressure, and then the pressure was gradually increased to 5.0 MPa. A synthetic air mixture was then added to the flowing methane to produce a reactant mixture of CH₄/air = 50/50 with a GHSV = 7,500 l/kg cat/hr. The temperature was increased at a rate of 2°K/min to a reaction temperature of 623K. At this temperature, 100% of the O₂ was converted to CO₂ and H₂O. Upon reducing the pressure to 0.1 MPa and continuing the test at 623K, the same catalytic activity and selectivity were observed. These results are shown in Figure

12 as the large filled symbols, where the rest of the data points were obtained from a study of 0.12 g of the same Pd(DAc)₂/SiO₂ catalyst tested in a microreactor system as indicated in Figure 7.

Since the lower gas flow (and higher residence time) in the larger high pressure reactor might enhance secondary reactions over the catalyst, e.g. decomposition of formaldehyde and methanol that might be formed by the selective oxidation of methane, the decomposition of methanol in the absence of methane and oxygen was investigated. It has previously been shown that passing methanol over a γ -alumina catalyst in a Pyrex reactor at 573K, ambient pressure, and a flow rate of 1.9 kg/kg cat/hr (stated elsewhere in the paper as 0.19 kg/kg cat/hr) did not result in the decomposition of the methanol but that the acidic alumina caused the transformation of part of the methanol into dimethylether (16). In that study, the addition of 0.5 wt% Pd to the alumina caused 63 mol% of the methanol to be converted to CO at the reaction conditions given above (dimethylether was still formed).

The decomposition of methanol was studied over 1.0 g of the 1.0 wt% Pd/SiO₂ catalyst at 0.1 and at 5.0 MPa (1 and 50 atm, respectively) pressure using a nitrogen carrier gas. This reaction is represented by Equation 8.



where the products are hydrogen and carbon monoxide (synthesis gas). The individual tests are summarized in Table 1. As can be seen, the sequence of experiments was

- i) temperature dependence at 0.1 MPa,
- ii) temperature dependence at 5.0 MPa, and
- iii) flow rate dependence at 5.0 MPa and 598K.

In the temperature dependence studies, the flow rates of nitrogen and

methanol were maintained constant, while in the flow rate dependence study the flow rates of both were increased and decreased in parallel. The extent of the transformation of CH_3OH into CO as a function of temperature is shown in Figure 13. It is clear that increased pressure inhibited the decomposition of methanol into carbon monoxide and hydrogen. In this pressure range (0.1 to 5.0 MPa), there is a 100K window ($\approx 575\text{K}$ at 0.1 MPa and $\approx 675\text{K}$ at 5.0 MPa) where the methanol was completely decomposed to synthesis gas over this catalyst.

In the flow rate dependence study, the flow rates of the nitrogen carrier gas and the methanol reactant were varied in concert. As shown in Figure 14, as the flow rates of the two components were increased, the % conversion of methanol to carbon monoxide decreased. However, the yield of CO , expressed as kg/kg cat/hr , was hardly affected under these reaction conditions and increased only slightly as the total gas hourly space velocity (GHSV) was increased, as shown in Figure 15.

The lower GHSV data point in Figure 15 (and highest methanol conversion data point in Figure 14) corresponding to $3.0 \text{ l N}_2/\text{hr}$ and $0.78 \text{ l CH}_3\text{OH}/\text{hr}$ was the last data point obtained in this study (see Test 13 in Table 1). During this last test, it was observed that the catalytic activity was higher than it was under comparable experimental conditions during the series of temperature dependence tests. The reason for this enhanced activity is unknown at the present time.

This study has demonstrated that in the absence of methane, oxygen, and water (free availability of the catalyst surface), methanol is readily decomposed at temperatures $>475\text{K}$ over a 1 wt% Pd/SiO_2 catalyst in our reaction system and that elevated pressures retard the decomposition reaction.

Conclusions. It has been shown that the Pd/SiO₂ catalyst is an active catalyst for oxidation of methane and for the decomposition of methanol under mild reaction conditions. For the oxidation of methane, the surface of the palladium catalyst exists in an intermediate oxidation state containing an optimum coverage of oxygen. Selectivity to partial oxidation products is enhanced by the deposition of small amounts of chlorine on the surface, which can be accomplished by the addition of small amounts of dichloromethane in the reactant gas mixture. The enhanced selectivity might arise by an ensemble-control exerted by the partial coverage of the surface by chlorine. Addition of water to the reactants induces a similar behavior to be observed. However, passing too much dichloromethane or water over the catalyst results in greatly suppressing the overall catalytic activity, and higher temperatures are needed to observe appreciable degrees of conversion of methane, which in turn causes a decrease in the selectivity to partial oxidation products. In studying the decomposition of methanol, a potential partial oxidation product of methane oxidation, over the Pd/SiO₂ catalyst in a large volume reactor, it was shown that elevated pressure and gas flows decreased the rate of methanol decomposition. Thus, reaction engineering of the oxidation of methane over palladium-based catalysts should be carried out such that the yields of selective oxidation products can be enhanced by balancing the reaction temperature with surface reactant and promoter concentrations, reactor pressure, and reactant gas flow.

REFERENCES

1. Klier, K., Herman, R. G., Simmons, G. W., Lyman, C. E., Santiesteban, J. G., and Najbar, M., in "Proc. 7th Indirect Liquefaction Contractors' Review Meeting, Volume II," U. S. Department of Energy, Pittsburgh Energy Technology Center, December 8-9, 1987, Pittsburgh, PA, pp 151-257 (1988).
2. Klier, K., Herman, R. G., Nunan, J. G., Smith, K. J., Bogdan, C. E., Young, C. W., and Santiesteban, J. G., in "Methane Conversion," ed. by D. M. Bibby, C. D. Chang, R. F. Howe, and S. Yurchak, Elsevier, Amsterdam, 109-125 (1988).
3. Santiesteban, J. G., Bogdan, C. E., Herman, R. G., and Klier, K., Proc. 9th Intern. Congr. Catal., 2, 561 (1988).
4. Bogdan, C. E., Nunan, J. G., Santiesteban, J. G., Herman, R. G., and Klier, K., in "Catalysis-1987," ed. by J. W. Ward, Elsevier, Amsterdam, 745-760 (1988).
5. Sofranko, J. A. and Jones, C. A., U. S. Patent 4,544,784 (Oct. 1, 1985); assigned to Atlantic Richfield.
6. Medvedev, S. S., Trans. Carov Chem. Inst., 4, 117-125 (1925); Chem. Abstr., 20, 2273 (1926).
7. Magee, E. M., U. S. Patents 3,014,969 (Dec. 26, 1961) and 3,032,588 (May 1, 1962); assigned to Esso Research and Engineering Co.
8. Cullis, C. F., Keene, D. E., and Trimm, D. L., J. Catal., 19, 378 (1970).
9. Mann, R. S. and Dosi, M. K., J. Chem. Tech. Biotechnol., 29, 467 (1977).
10. Anderson, J. R. and McConkey, B. H., J. Catal., 11, 54 (1968).
11. Pitchai, R. and Klier, K., Catal. Rev.-Sci. Eng., 28, 13 (1986).
12. Klier, K., Simmons, G. W., Herman, R. G., Reuter, M., Wang, Y.-N., and Marcos, J., "Mechanisms and Controlling Characteristics of the Catalytic Oxidation of Methane," Final Technical Report DOE/ER/13090-F to the U. S. Department of Energy, Contract No. DE-AC02-83ER13090, 78 pp (Nov. 1987).
13. Klier, K., Marcos, J., Simmons, G. W., and Wang, Y.-N., "Adsorption of Dichloromethane and Its Interaction with Oxygen on the Pd(100) Surface: The Effect of a Cl Layer on O Chemisorption and Oxidation of C Residues," to be submitted.
14. Klier, K., Herman, R. G., Simmons, G. W., Najbar, M., and Santiesteban, J. G., Quarterly Technical Progress Report DOE/PC/80014-5 to the U. S. Department of Energy (March 1987).

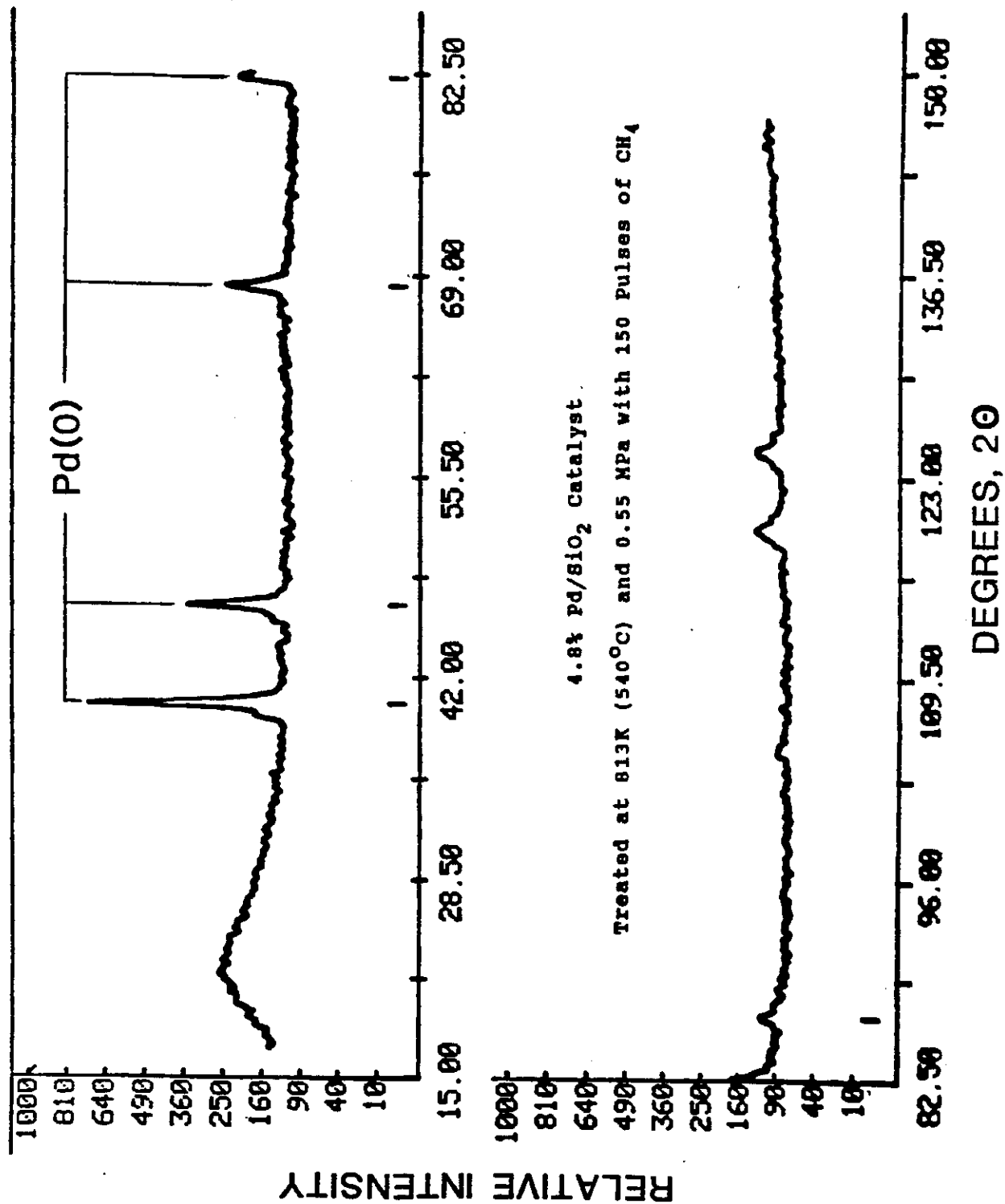
15. Klier, K., Herman, R. G., Simmons, G. W., and Najbar, M., Quarterly Technical Progress Reports DOE/PC/80014-6 (June 1987) and DOE/PC/80014-8 (November 1987) to the U. S. Department of Energy.
16. Wickham, D. T., Logsdon, B. W., and Cowley, S. W., Preprint, Div. Fuel Chem., ACS, 31(3), 124 (1986).

TABLE 1

Experimental conditions employed in the investigation of the decomposition of methanol to synthesis gas over a 1.0 wt% Pd/SiO₂ catalyst (1.0 g) carried out by injecting methanol into a nitrogen carrier gas.

Test	Temperature (K)	Pressure (MPa)	Flow Rates	
			N ₂ (l/hr)	CH ₃ OH (mol/hr)
1	415	0.1	3.0	0.032
2	423	0.1	3.0	0.031
3	480	0.1	3.0	0.031
4	529	0.1	3.0	0.032
5	573	0.1	3.0	0.032
6	415	5.0	3.0	0.032
7	473	5.0	3.0	0.031
8	573	5.0	3.0	0.032
9	623	5.0	3.0	0.033
10	648	5.0	3.0	0.033
11	598	5.0	6.0	0.063
12	598	5.0	12.0	0.119
13	598	5.0	3.0	0.033

FIGURE 2



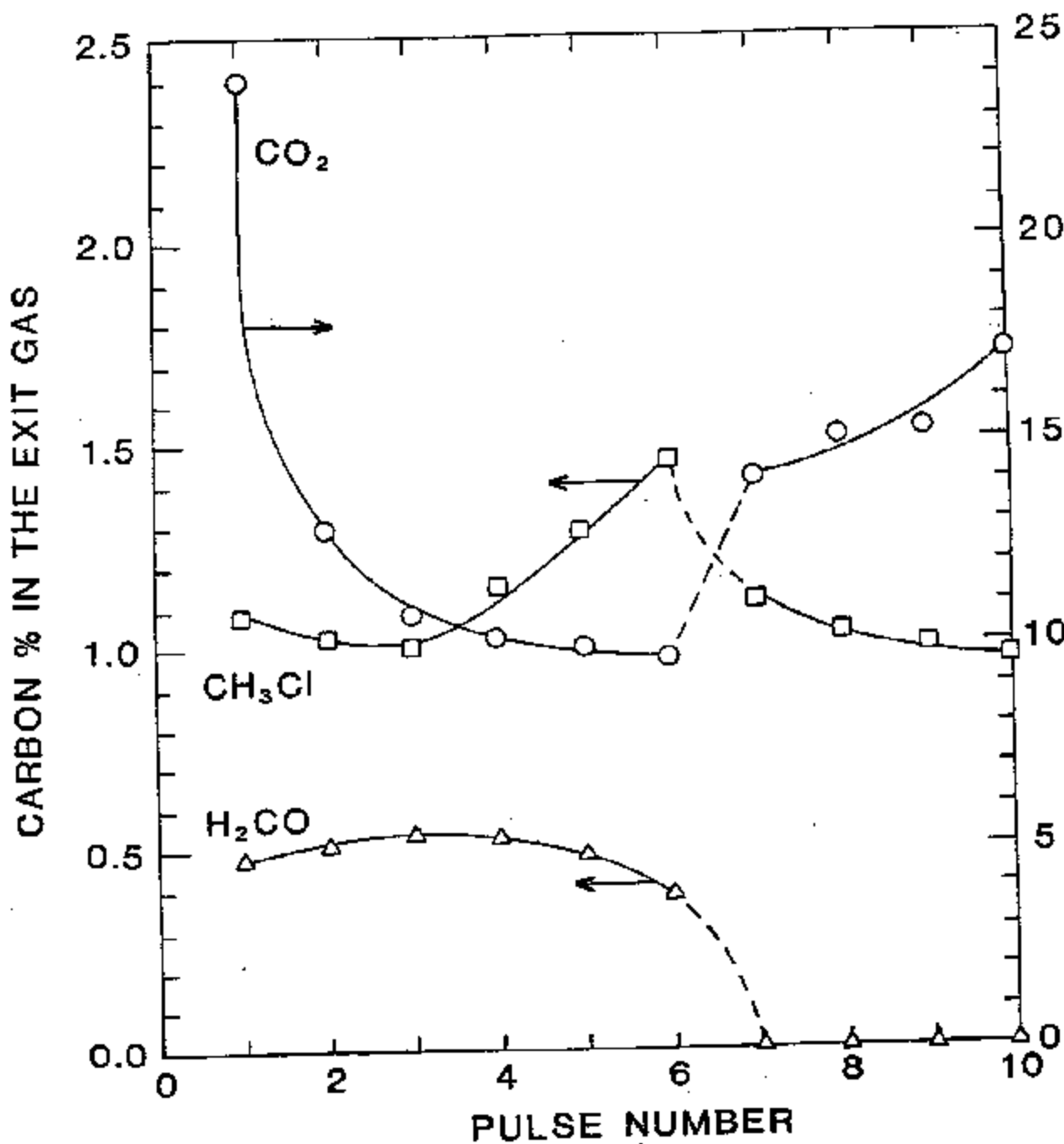


FIGURE 3. Product Selectivities Observed During Six Pulses of CH₄ + O₂ + CH₂Cl₂ - 1/2/0.2 Over the 4.8 wt% Pd/SiO₂ Catalyst at 648K. Followed by Four Pulses in which the Dichloromethane was Replaced by N₂.

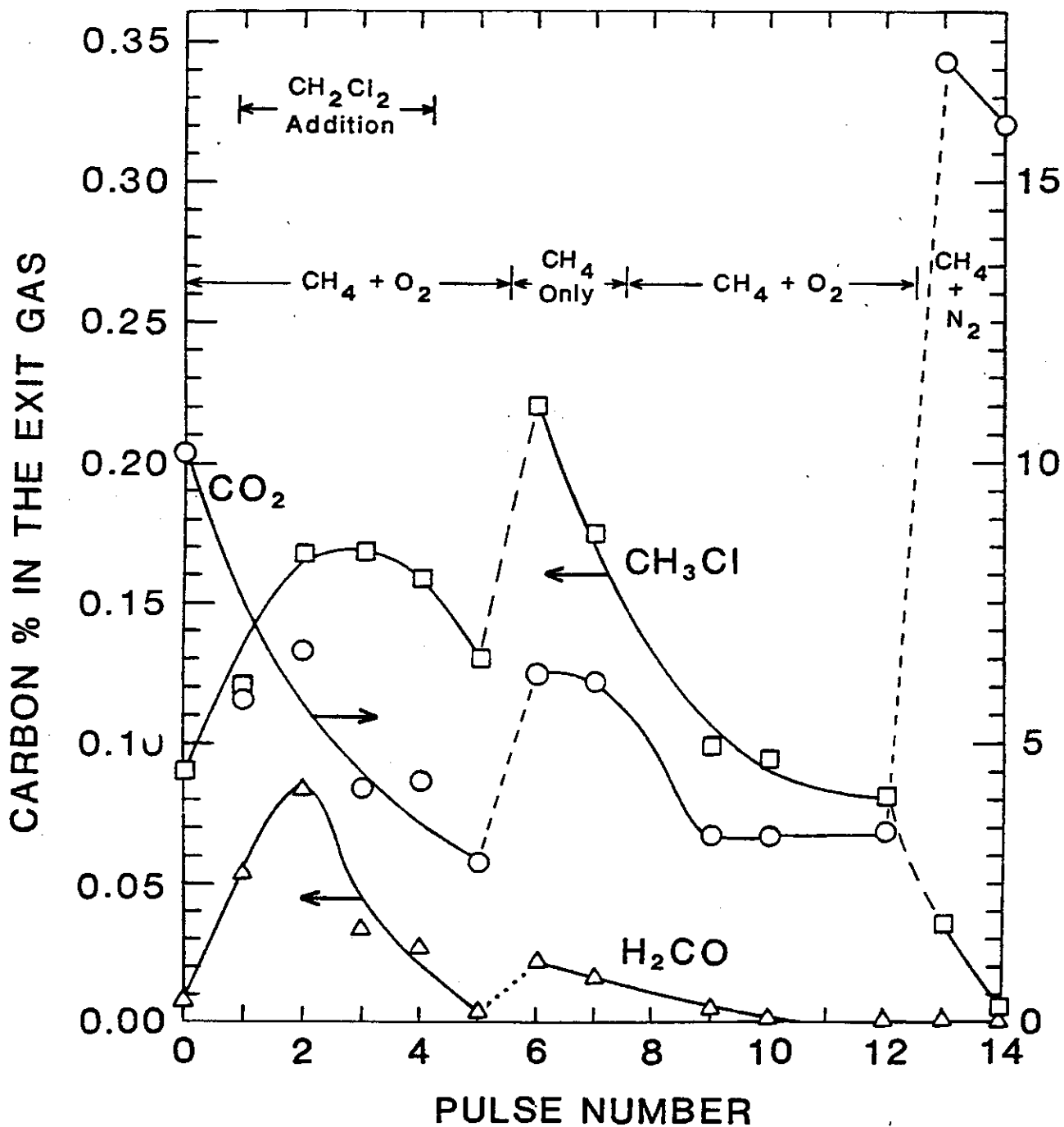


FIGURE 4. Product Selectivities Observed Over the 4.8 wt% Pd/SiO₂ Catalyst During and After the Addition of Dichloromethane to Pulses of Methane/Oxygen (CH₄ + O₂ + CH₂Cl₂ = 1/2/0.015) at 761 K. Pulses of Neat Methane Increased the Yield of All Three Products.

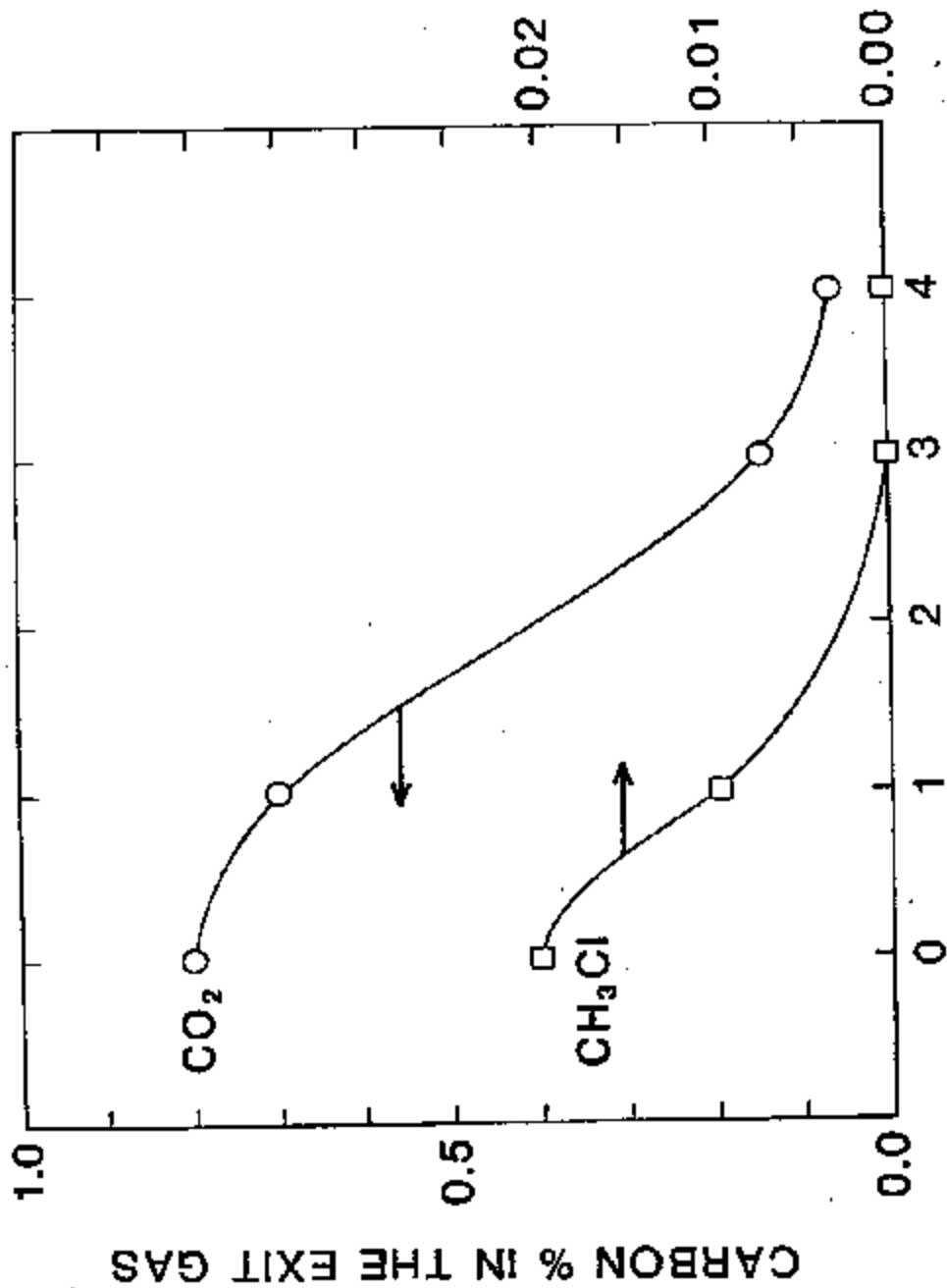


FIGURE 5. The Effect of Water on the Conversion of Methane to Carbon Dioxide and Chloromethane Over the 4.8 wt% Pd/SiO₂ Catalyst at 648 K. The Reactant Mixture Pulsed into the Reactor Consisted of CH₄ + O₂ + H₂O = 1:2:0.02%.

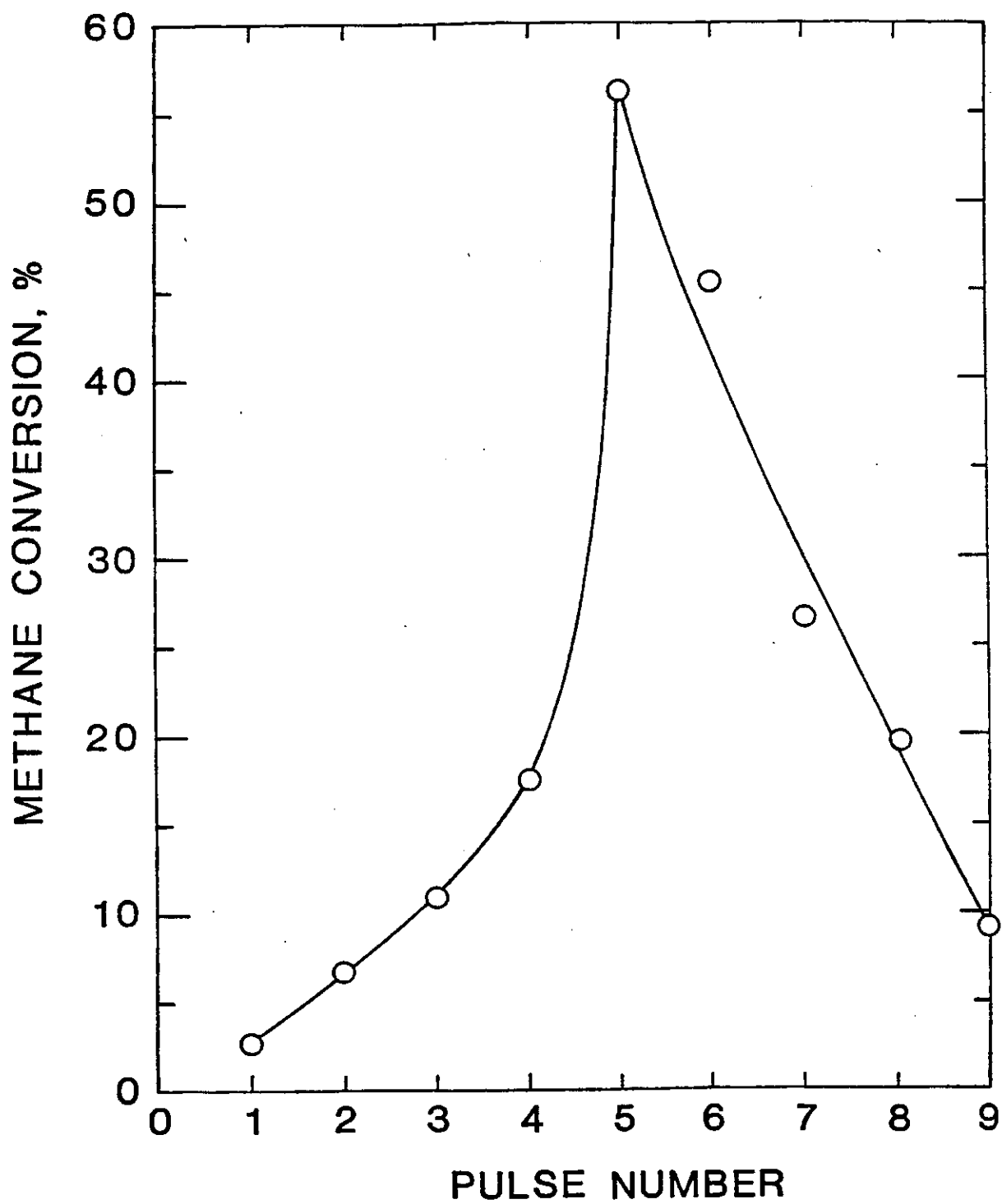


FIGURE 6. The Conversion of Methane to Carbon Dioxide as a Function of the Number of Pulses of Methane Passed Over an Oxygen-covered Pd/SiO₂ Catalyst (4.8 wt% Pd) at 544K.

METHANE OXIDATION OVER 1 wt% Pd/SiO₂
CH₄/O₂/N₂ = 1.0/0.26/0.84, 0.1 MPa
GHSV = 85,000 l/kg cat/hr

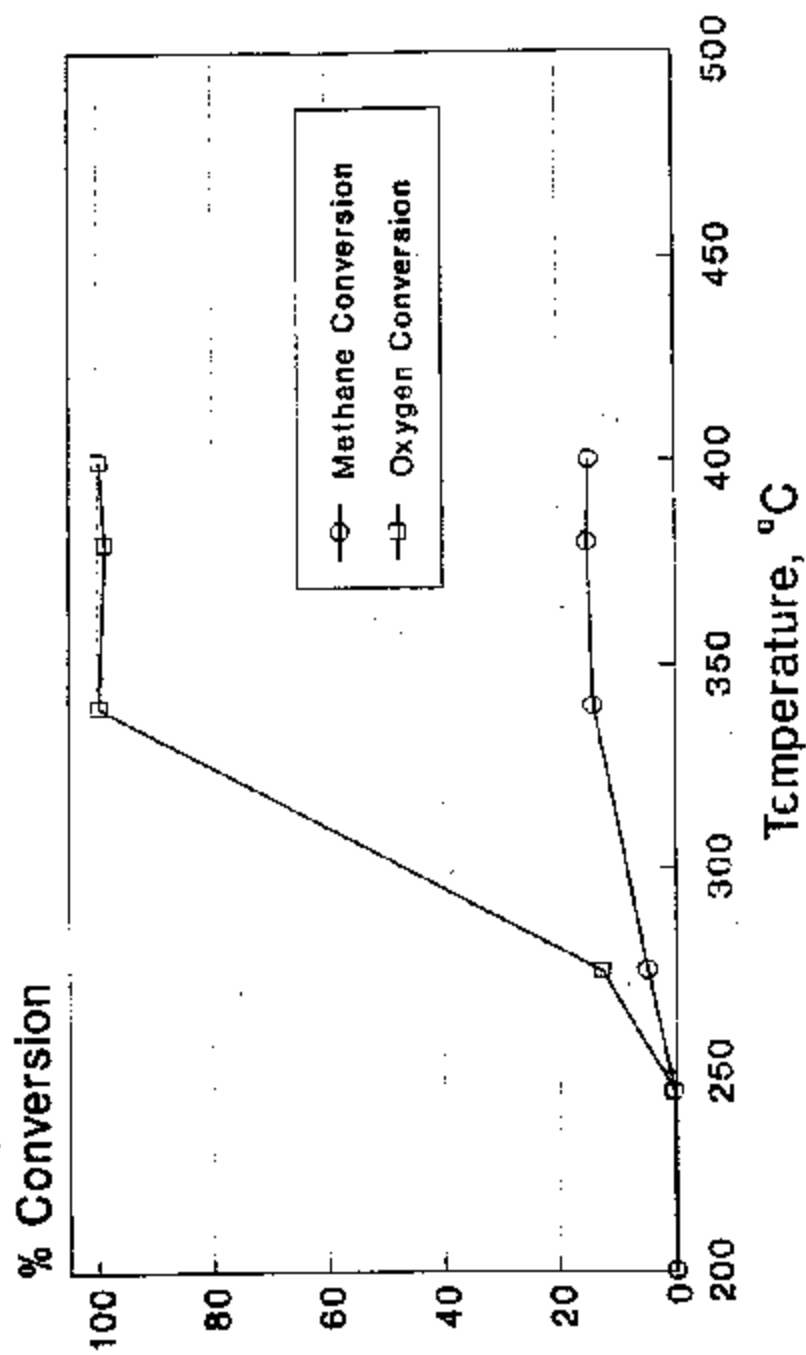


FIGURE 7

METHANE OXIDATION OVER 1 wt% Pd/SiO₂
CH₄/O₂/N₂ = 1.0/0.26/0.84, 0.1 MPa
GHSV = 85,000 l/kg cat/hr

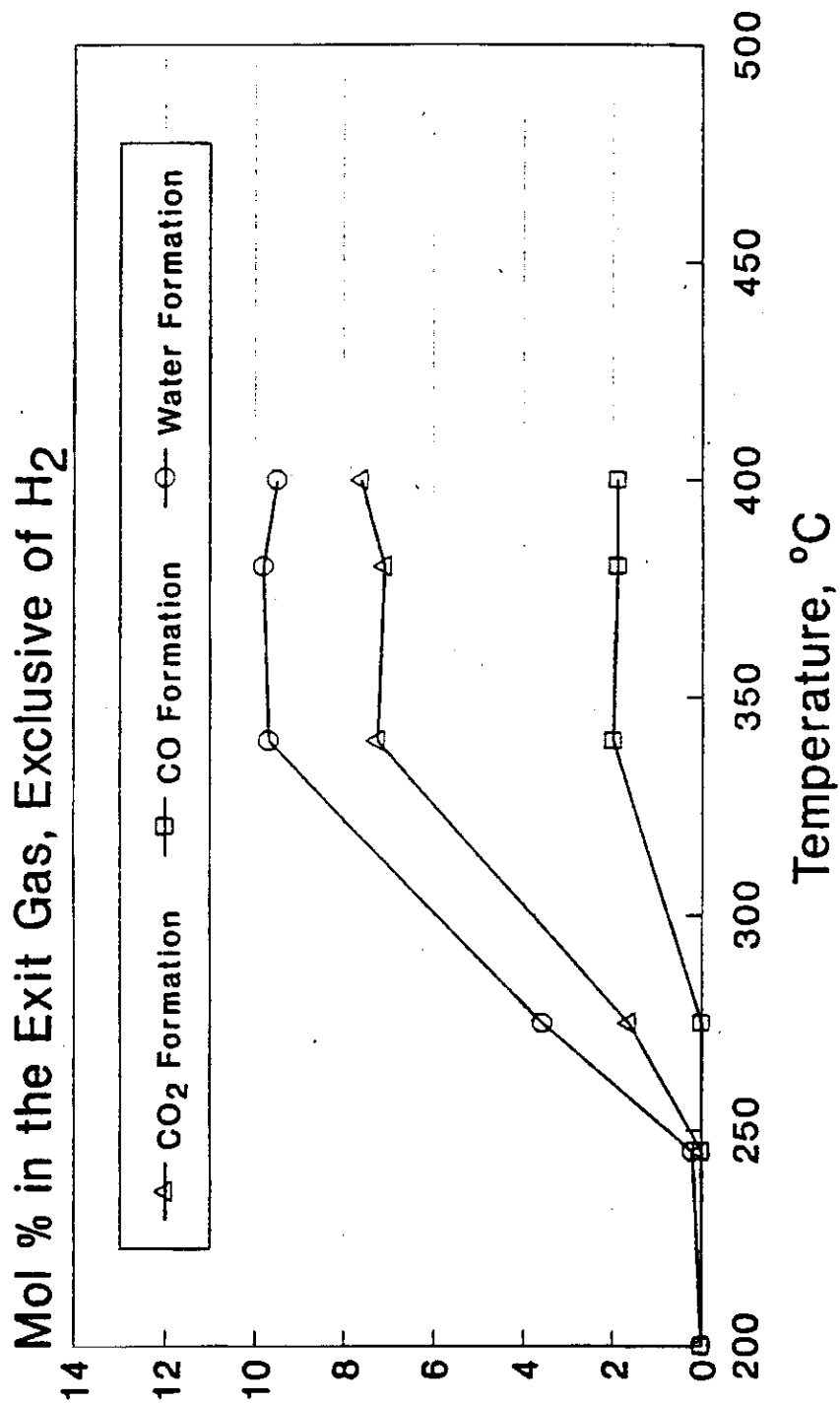


FIGURE 8

METHANE OXIDATION OVER 1 wt% Pd/SiO₂

Water Addition (3.8 %), 0.1 MPa

CH₄/O₂/N₂/H₂O = 1.0/0.26/0.84/0.085

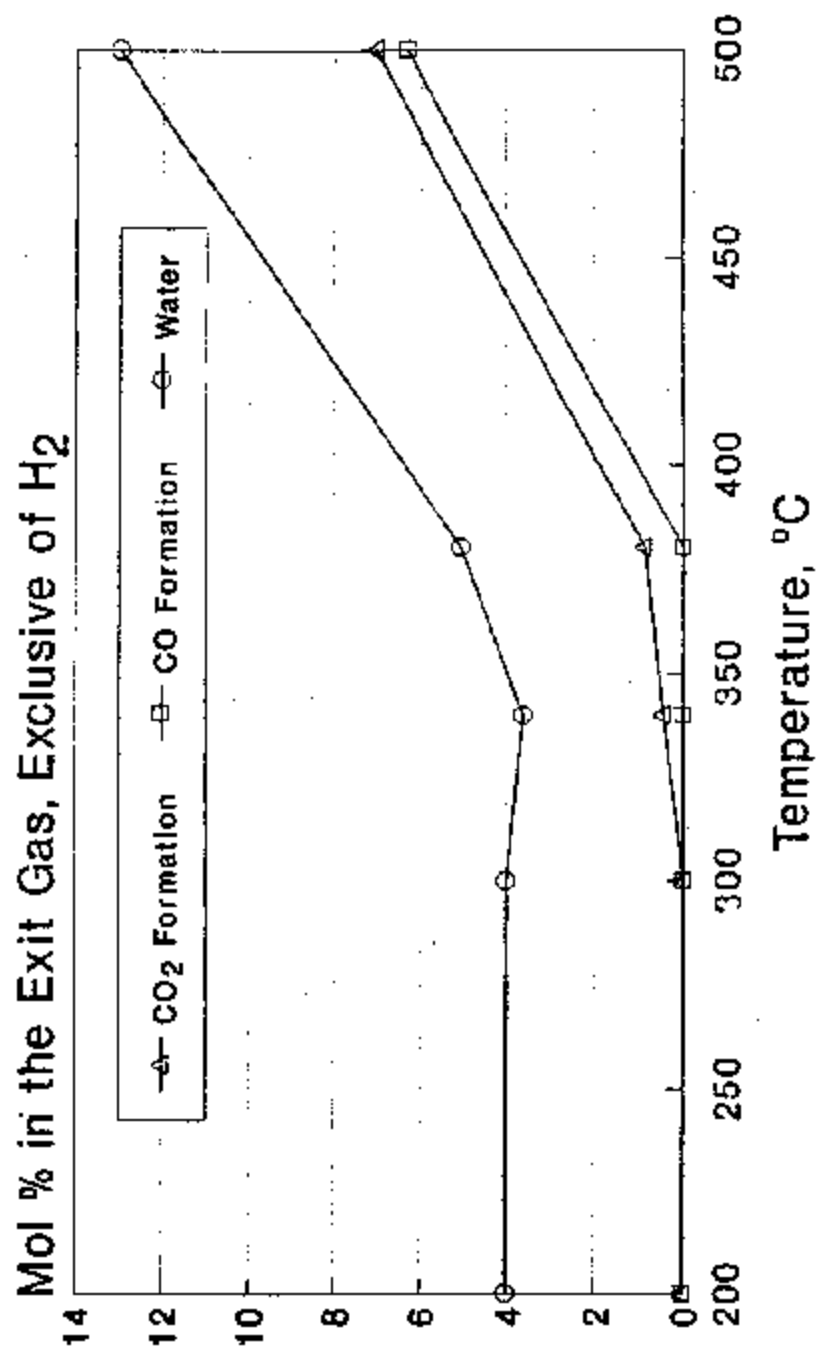


FIGURE 9

METHANE OXIDATION OVER 1 wt% Pd/SiO₂
 Dichloromethane Addition (2.0 %), 0.1 MPa
 $\text{CH}_4/\text{O}_2/\text{N}_2/\text{CH}_2\text{Cl}_2 = 1.0/0.26/0.84/0.04$

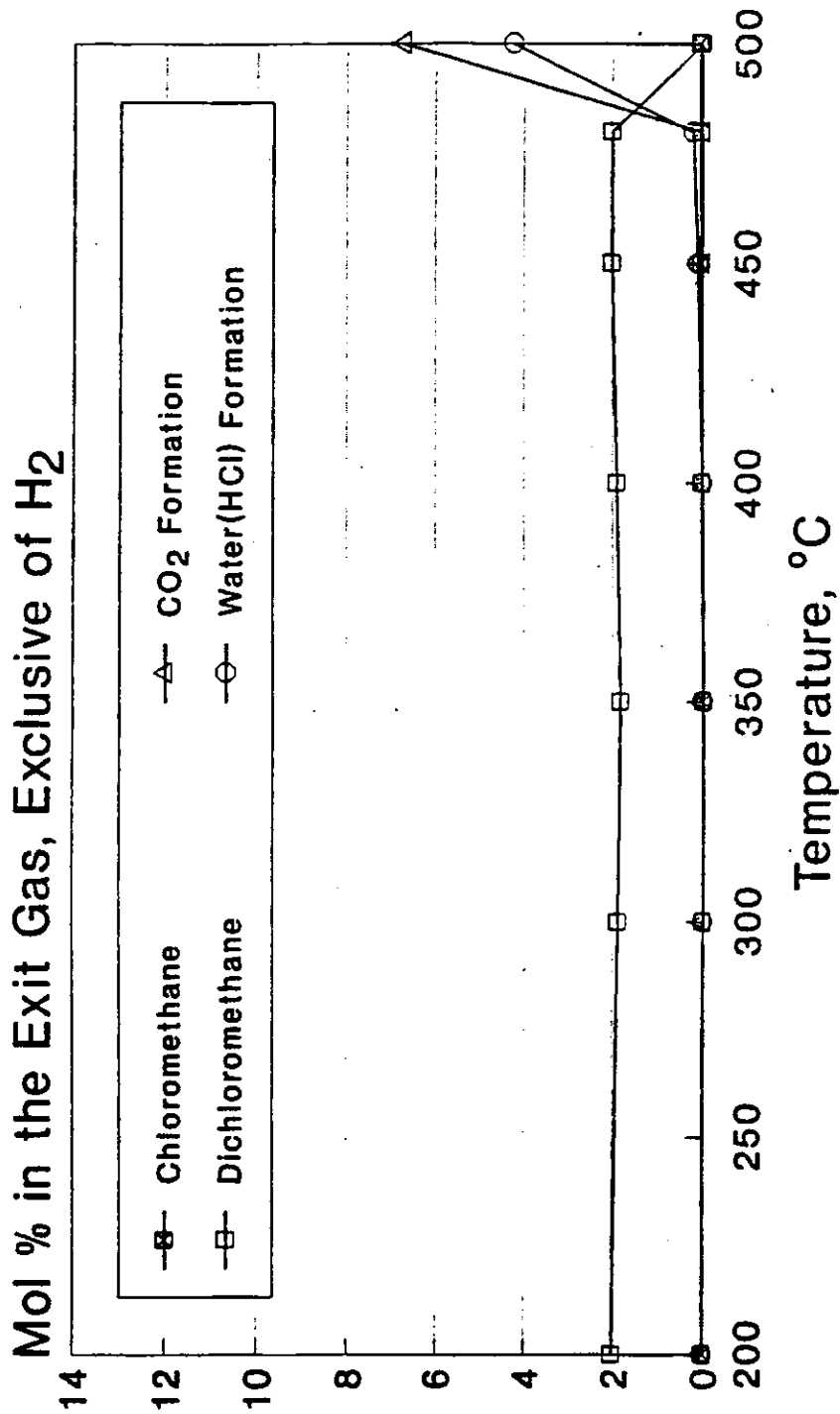
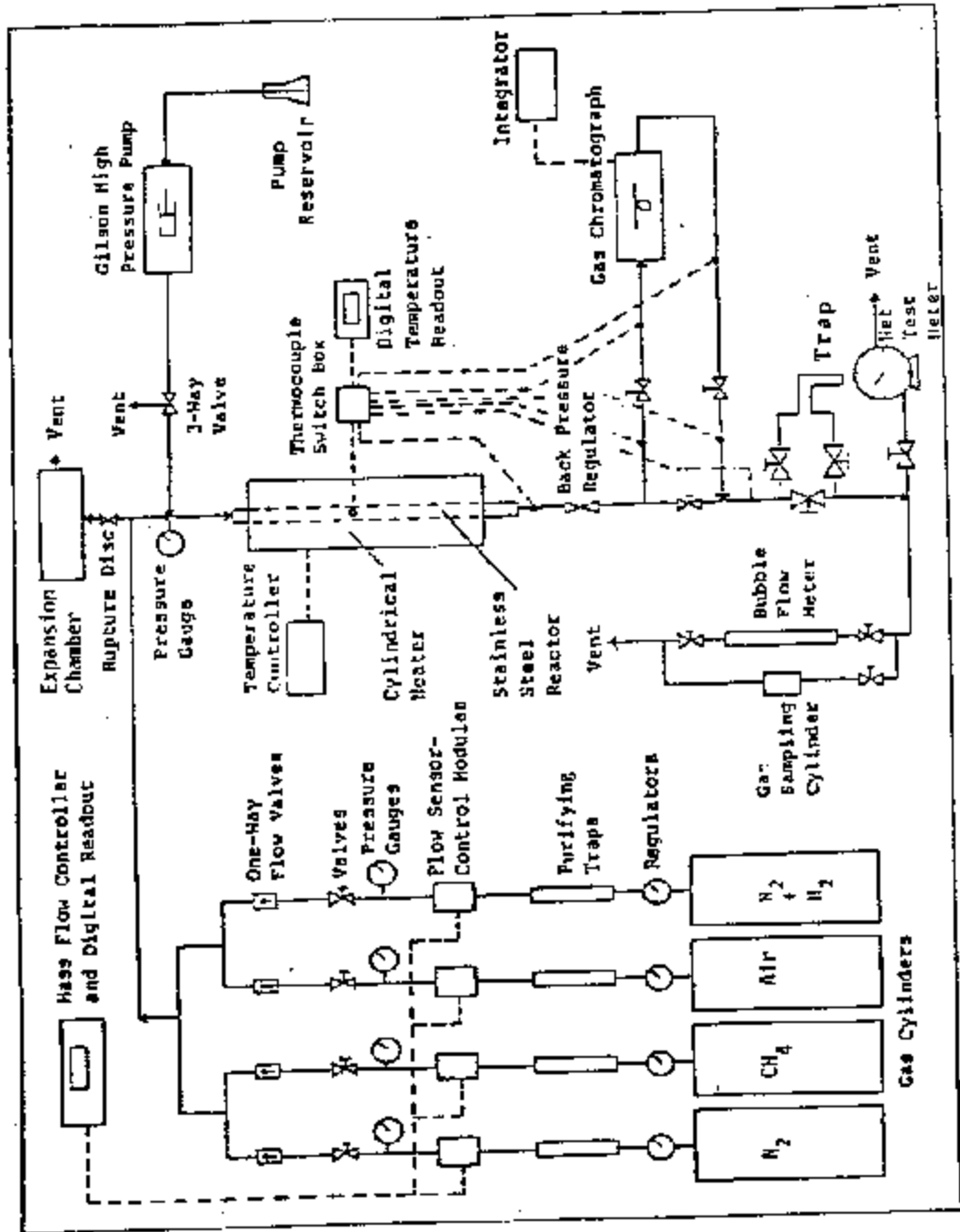


FIGURE 10

FIGURE 11

SCHEMATIC OF THE HIGH PRESSURE METHANE OXIDATION REACTOR SYSTEM



METHANE OXIDATION OVER 1 wt% Pd/SiO₂
CH₄/O₂/N₂ = 1.0/0.26/0.84, 0.1 MPa
GHSV = 85,000 l/kg cat/hr

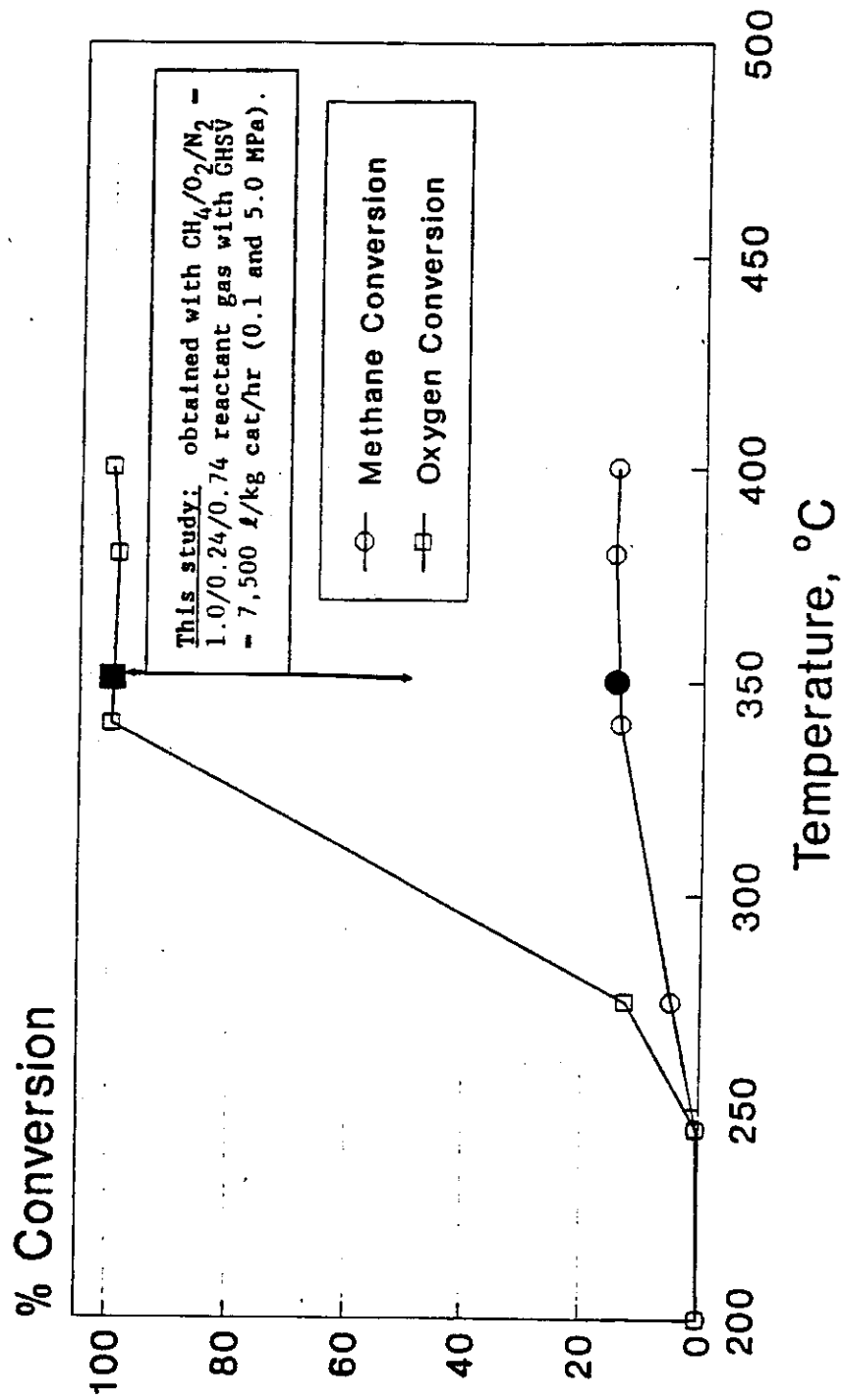


FIGURE 12

METHANOL DECOMPOSITION OVER 1.0 g Pd/SiO₂ (3 l/hr N₂)

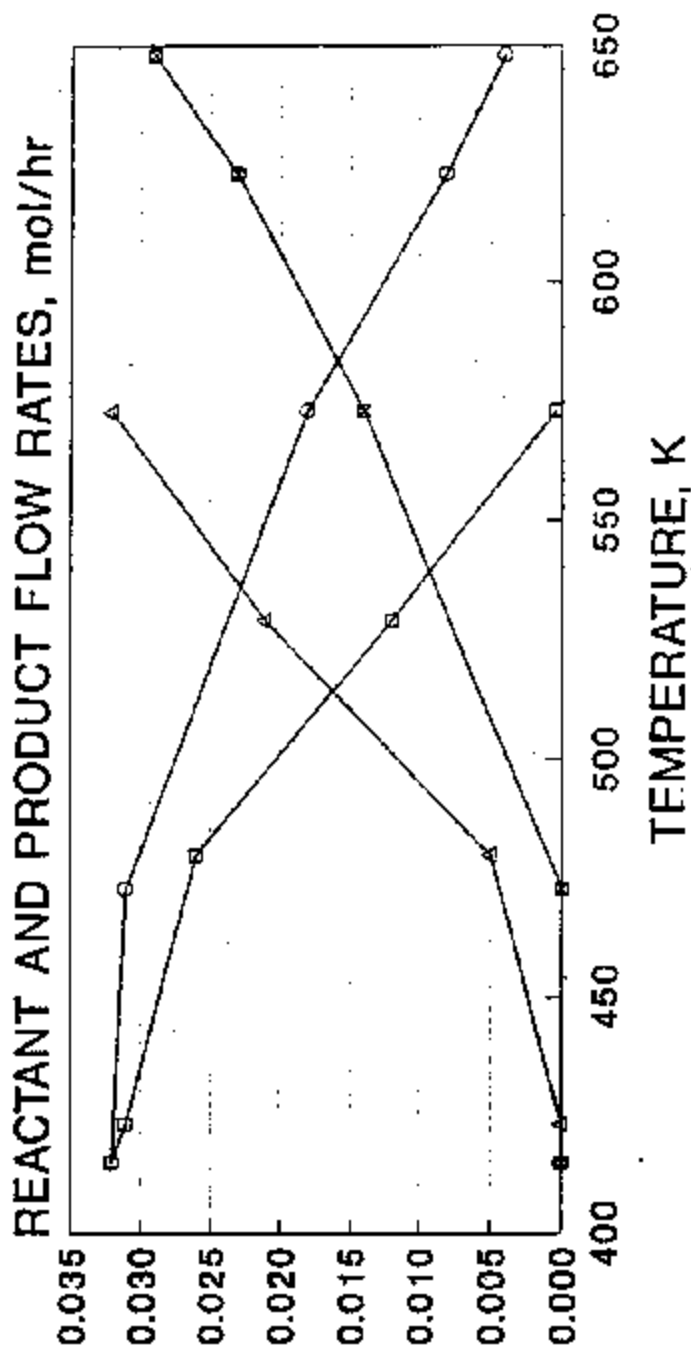


FIGURE 13

FIGURE 14

METHANOL DECOMPOSITION
CH₃OH Injected into N₂ at 5.0 MPa
and 598K over 1.0 g Pd/SiO₂

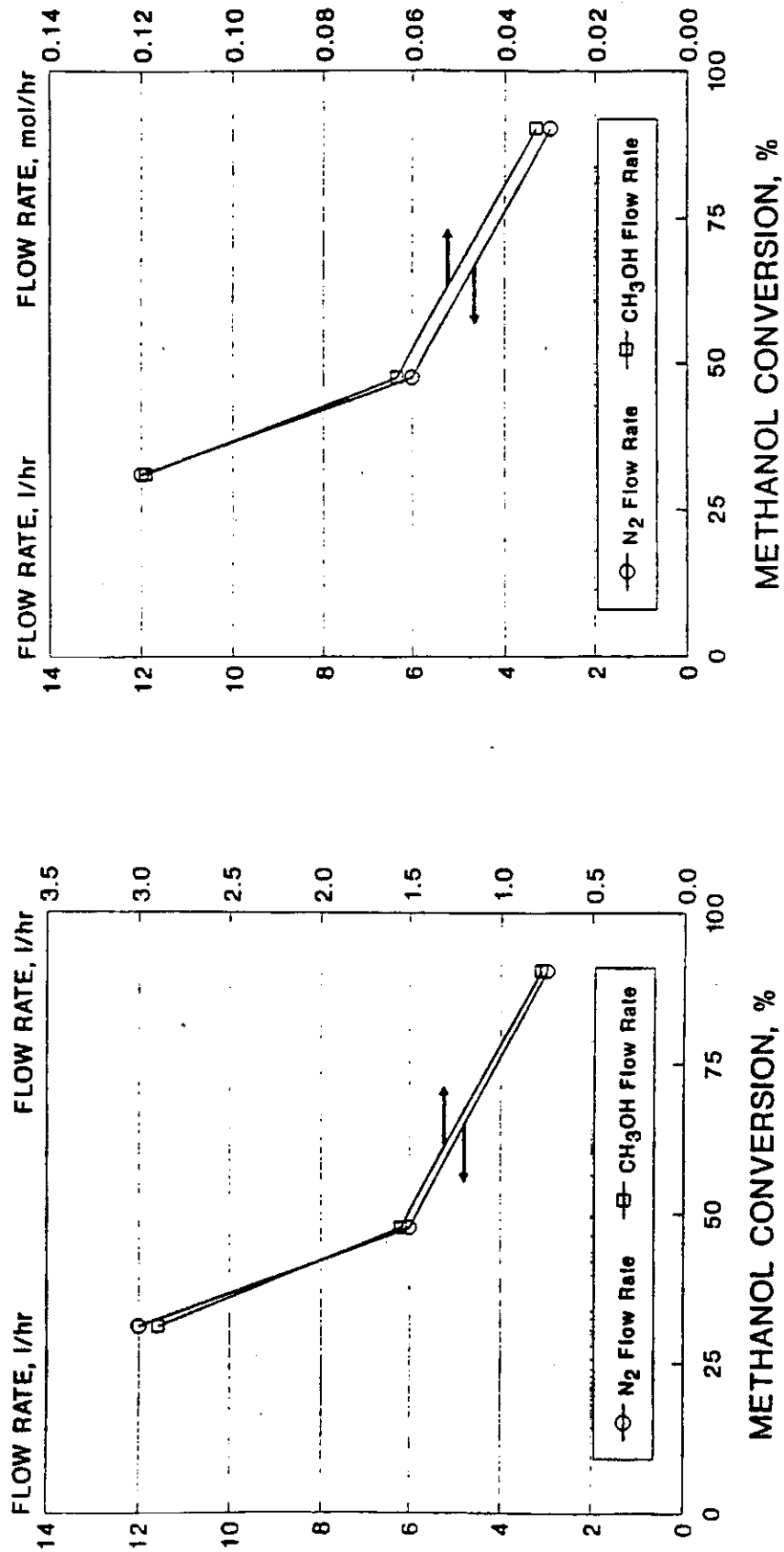


FIGURE 15

METHANOL DECOMPOSITION
IN N₂ CARRIER GAS AT 5.0 MPa
AND 598K OVER 1.0 g Pd/SiO₂

